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A STUDY OF THE ADSORPTION FROM SOLUTION FROM THE
STANDPOINT OF CAPILLARITY

DISSERTATION

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Doctor of Philosophy

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A STUDY OF THE ADSORPTION FROM SOLUTION FROM THE STANDPOINT OF CAPILLARITY

INTRODUCTION

By solubility, one ordinarily means the maximum amount of a pure substance that another pure substance has the power of assimilating homogeneously, under given conditions of pressure, temperature etc. That is to say, we look upon a substance - say a liquid - as having a certain "power" to take up another substance to form a homogeneous solution. A little thought, however, leads us to the fact that solubilities, as ordinarily expressed in tables, do not give us any idea as to the magnitude of this particular "power" in question for a pure substance; for, as soon as some molecules of A are taken up by B, then the "solution power" is not a characteristic of pure B, but of B containing some A. A little later, as equilibrium is being approached, the solution power is characteristic of a still different system. Thus, solubility as it is usually expressed, gives us the magnitude of a very complex function.

We may now ask the question: What would be the solubility of B in A, provided once the molecules of B arrive in A they have no longer any effect whatsoever upon molecules of B, - that is to say, provided the thermodynamic environment of A remains constant? In other words, this would be correcting

the ordinary solubility value for the amount of solute which is attracted into a solution by the solute particles already in the solution. In this light, it would be expected that liquids, for example, which are considered as infinitely miscible, have really a definite tendency to dissolve in each other.

Just how this quantity might be measured will be explained below from the standpoint of certain adsorption formulae. We shall call this new value for solubility, then, the "solution power" or S_0 , although, as will be seen below, it is sometimes rather difficult to ascribe a definite physical meaning to this quantity.

It is well known that liquid in a capillary tube has very different physical properties from the liquid as it ordinarily exists with a plane surface. Having a concave upward surface, the vapor pressure, as well as the solubility (or tendency to dissolve) is much lower. Now there is much evidence to warrant the belief that silica gel consists of very fine pores¹, that it is nothing but a net-work of capillaries. A substance such as water, which wets this gel, when in the capillaries would have a less solubility in some other liquid than if the

1. Patrick S. McLaughlin, J. Am. Chem. Soc. 42, 946 (1920)

water were merely allowed to dissolve in this liquid from a plane surface. Or, what is saying the same thing, in a solution of water in some liquid should be subjected to a capillary system such as silica gel, a certain amount of the water would be "adsorbed" in the capillaries of the gel. That is to say, a new phase separates out, and thus the concentration in the original phase is much lower than before the capillary system was applied. Knowing this "lower" concentration, it is then possible to calculate, by certain adsorption formulae, the value of the theoretical quantity - S_0 .

If the above ideas be correct, not only do miscible liquids have a definite "solubility" in each other, but liquids showing a critical solution temperature should show "adsorption" - as above defined - at temperatures somewhat above the critical solution temperature. In other words, in capillaries, critical solution temperatures are higher than those ordinarily given. This point will be considered in detail later.

THEORETICAL CONSIDERATIONS

Patrick and McCavack¹ have explained the adsorption of sulfur dioxide by silica gel on the basis of the empiric relation

$$V = K \frac{P}{P_0}$$

where

V = volume of liquified sulfur dioxide per gram gel

P = pressure of sulfur dioxide at equilibrium

P₀ = saturation pressure at the temperature

σ = surface tension at the temperature

This relation has been subsequently found to hold for the adsorption of ammonia, carbon dioxide, butane, nitrous oxide, and also for the solution of ammonia in water². In all cases we have merely a liquid filling up the pores of a number of capillary tubes. In the case of ammonia in water, the ammonia is considered as existing as a liquid when in "solution" in water.

Considering, however, adsorption (or capillary condensation) not from a gas - where the vapor pressure in the capillaries is lowered - but of a solute from a solution where the

1. Loc. cit.

2. Neuhauser & Patrick, J. Phys. Chem. 25, 695 (1921)

solubility is lowered, our formula would read, analogously

$$V = K \frac{S}{S_0}$$

where S is the equilibrium concentration in the original phase, and S_0 is the theoretical quantity above discussed. It is to be expected that S_0 would be less than the ordinary solubility inasmuch as the solute particles in the solvent are considered as having no more effect on other solute particles in the solvent, as explained before.

The analogy between solubility and pressure may be made clear by the following: in a capillary tube, a liquid is capable of existing under a vapor pressure much less than the ordinary vapor pressure over the liquid at the temperature; likewise in a capillary tube, a liquid can exist in contact with a solution of it in some solvent, which solution is of a much less concentration than would be attained ordinarily with practically plane surfaces. In this manner, S_0 is to be considered as "analogous" to P_0 .

It may be argued that S_0 should come out as ordinary solubility, inasmuch as gas laws apply to solutions. This may be the case with liquids, then, which are only very slightly miscible; but with the liquids used below, namely n-butyl alcohol and water, the water dissolves in the alcohol to the extent of 20%. With liquids slightly miscible, the value of S_0 , as

found above, should be nearer to the ordinary solubility than in the case of liquids which are miscible in large proportions. Likewise, S_0 of liquids miscible in "all" proportions, would be still further away from the ordinary solubility which in the latter case would be infinity.

Now, before the above formula was applied to the system n-butyl alcohol - water in order to solve for S_0 , it was first necessary and advantageous to obtain the formula from theoretical considerations. A very rigorous formula, similar to the above, can be obtained by the combination of two other formulae. The relationship upon which the empiric formula written above is really based, is the familiar capillary - radius - pressure formula:

$$\ln \frac{P_0}{P} = \frac{2 \sigma M}{D r RT} \quad \text{----- (1)}$$

derived from thermodynamics. Here

- P_0 = vapor pressure over flat surface
- P = vapor pressure over curved surface
- σ = surface tension
- M = molecular weight
- D = density liquid
- r = radius of capillary (or radius of curvature)
- R = gas constant in dynes-cm. per degree
- T = absolute temperature

The vapor is assumed to obey the gas laws.

A more rigorous equation is:

$$r = \frac{2 \sigma M}{RT D \ln \frac{P_0}{P} - P_0 M} \quad \text{-----} \quad (2) \quad *$$

Now these formulae could be related to the volumes of liquids adsorbed by capillaries if we knew the relation between the volume and the radius. Inasmuch as the pores or capillaries of silica gel are considered conical, we do not have a system of constant radius. A more or less general relationship would be

$$V = K r^3 \quad \text{-----} \quad (3)$$

Thus for each volume of liquid adsorbed per gram of gel (V) there would correspond a certain radius. It must be remembered, however, that with silica gel, this represents an "average" radius, inasmuch as we have conical pores.

Now from the above expression we obtain the variation of the volume with the radius,

$$dV = \frac{K}{n} r^{n-1} dr \quad \text{-----} \quad (4)$$

and from equation (1) we obtain the variation of the vapor

1. Anderson, Zeit. Phys. Chem. 88, 191 (1914).

pressure with the radius,

$$(5)$$

Combining equation (4) and (5) we eliminate dr , and obtain

$$(6)$$

which upon integration gives

$$(\text{integration constant}) \text{---} (7)$$

When $P = P_0$ we have saturation, and the volume then is equal to the total internal volume of the gel (V_0).

Therefore

$$V = V_0 \quad \text{and}$$

$$(8)$$

represents the complete relation between P and V .

According to the more rigorous Hinkowski formula (2), the relation is

$$(9)$$

Inasmuch as K is very large, the last term can always be neglected as will be shown later in the calculations. K also appears in the first term on the right, but here R is also very large (8.5×10^7).

This formula (8) can now be tested by results on the adsorption of sulfur dioxide. In order to see if K and $\frac{1}{n}$ are constant, r is first found from equation (1), slightly transformed:

$$r = \frac{2.303 M 10^7 (.4543)}{D RT \log \frac{P}{P_0}} \quad \text{-----}(10)$$

The factor 10^7 is used in order that r may be expressed in g./cc. Values of $\log P/P_0$ were taken from article by Patrick and McCavack¹ from which $\frac{1}{n}$ and K are found.

1. Loc. cit. p. 976.

TABLE I

$\log \frac{P}{P_0}$	$\log V$	Temp.	$r(\text{cm})$	$\frac{1}{n}$	$K \times 10^{-6}$
1.06711	1.21580	30°	0.41	.879	.644
1.22883	1.23652	(near saturation)	—	—	—
1.16702	1.23355	40°	0.41	.916	.724
1.08077	1.21436	(near saturation)	—	—	—
2.50189	2.80302	100°	0.10	1.930	18.545
2.41060	2.75545	(near saturation)	—	—	—
2.06453	2.73400	50°	0.19	2.420	15.306
3.33415	3.39811	(far from saturation)	—	—	—
1.70435	1.57984	- 54°	2.57	0.363	0.539
1.49337	1.49485	(near saturation)	—	—	—

Here in a typical case

$$R = 82,156,000 \text{ dynes-degree}$$

$$D = 1.3596 \text{ at } 30^\circ$$

$$T = 303$$

$$\sigma = 22.75 \text{ dynes/cm.}$$

$$M = 64$$

From the above table, it is noticed that the values of $\frac{1}{n}$ and K are not such as to warrant their use as constants. A calculation was also made using the extra term of the more rigorous Minkowski formula (9), with the result that $\frac{1}{n}$ came out to be .921 instead of .916 for the 40° experiment, showing that it will not be necessary to use this term, considering the great complexity of the problem.

Inasmuch as the pressure - radius formula is a thermodynamic one, it was thought that probably the volume - radius relation assumed

$$V = K r^{\frac{1}{n}}$$

might not correctly represent the state of affairs in silica gel. In order to see the relation between the internal volume of the gel and the radius, values of volumes of sulfur dioxide, butane, and water adsorbed per gram gel (found by dividing mass adsorbed by the density of the liquid at the temperature) were plotted against the radii as found from the pressures, corresponding to the above volumes, by means of equation (10).

The results of these calculations are given in the following table and curves. The sulfur dioxide data are taken from Patrick and McDavock¹, the butane results from Long² and the water results from Spýrke³.

1. Loc. cit.
2. J. C. Long, Ph.D. Dissertation, 1921
3. J. S. Spýrke, Ph.D. Dissertation, 1922

TABLE II

Substance	Temp.	$\log \frac{P}{P_0}$	$r()$	V(cc)	Water content gel
Sulfur dioxide	300°	$\bar{3}.85415$	0.1589	.0250	4.87%
"	"	$\bar{2}.06453$	0.1913	.0543	"
"	"	$\bar{2}.57194$	0.2274-	.0771	"
"	"	$\bar{2}.60706$	0.2658	.1008	"
"	"	$\bar{2}.83983$	0.3161	.1294	"
"	"	$\bar{1}.06711$	0.3969	.1636	"
"	"	$\bar{1}.22883$	0.4801	.1934	"
"	"	$\bar{1}.51301$	0.5312	.2096	"
"	-80°	$\bar{2}.16943$	0.5166	.0885	"
"	"	$\bar{2}.21895$	0.8009	.1735	"
"	"	$\bar{1}.27300$	1.3011	.2395	"
"	"	$\bar{1}.33982$	2.0355	.3193	"
"	"	$\bar{1}.71728$	3.5457	.3629	"
"	"	$\bar{1}.97430$	3.7240	.4035	"
"	100°	$\bar{2}.03643$	0.0760	.0310	"
"	"	$\bar{2}.27363$	0.0664	.0458	"
"	"	$\bar{2}.41060$	0.0939	.0507	"
"	"	$\bar{1}.36189$	0.0996	.0635	"
"	-52°	$\bar{3}.63610$	0.3245	.0570	"
"	"	$\bar{2}.67313$	0.5733	.1497	"
"	"	$\bar{1}.04748$	0.7986	.2019	"
"	"	$\bar{1}.29332$	1.0041	.2613	"

TABLE II (con't.).

Substance	Temp.	$\log \frac{P}{P_0}$	$r(\text{cm})$	V(cc)	Water content rel
Sulfur dioxide	-54°	1.49337	1.3015	.3125	4.87%
"	"	1.70435	2.5730	.3801	"
Butane	30°	2.41274	0.3436	.0305	0.03%
"	"	1.10010	0.4287	.0949	"
"	"	1.46047	0.7168	.1836	"
"	"	2.85249	0.1801	.0145	1.96%
"	"	2.73868	0.3180	.0894	"
"	"	1.45038	0.7087	.1917	"
"	"	2.29366	0.3271	.0323	3.77%
"	"	1.11221	0.4357	.0873	"
"	"	1.43637	0.3703	.1749	"
"	100°	2.06562	0.0657	.0081	---
"	"	1.03639	0.0923	.0266	---
"	"	2.74599	0.1014	.0321	---
"	0°	1.52205	0.3044	.0449	---
"	"	1.19614	0.6019	.1927	---
"	"	1.62957	1.4310	.3542	---
"	"	1.33633	3.7340	.4320	---
Water vapor	30°	2.96379	0.4289	.0640	---
"	"	1.11613	0.3210	.0320	---
"	"	1.03443	1.3170	.2130	---
"	"	1.67394	1.3350	.2340	---
"	"	1.76139	1.9250	.1390	---
"	"	1.3013	3.1540	.2790	---

Cubic
centimeter
adsorbed
per gm.
gel (V)

4

3

2

1

Putane 0°

50° - 54°

50° - 80°

H₂O 30°

Putane 20° H₂O content 3.11%
1.9%
0.03%

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

A glance at the above data and accompanying curves shows many interesting and significant relations. First of all it shows that the curves cannot be represented by the relation

$$V = K r^{\frac{1}{n}}$$

until the radius reaches the value of about .5000 . Before this is reached, the curves have the form

$$V = K r^3$$

Thus the complete curves would require at least a cubic equation. Now, the shape of the curves is that which, upon the basis of the supposed structure of the gel, would be expected. At very low volumes, the capillary effects are very powerful, but the volumes corresponding to the radii would be very small - remembering that we have a conical "tube". As we fill up the V shaped capillary, the volumes become larger, but the capillary powers are becoming less, so that the curves eventually turn parallel to the r axis. Furthermore, the curves all are "aiming" at a value of about .4 cc for V, which is the value of the internal volume of the gel as found by Patrick and McLavack.

Of course, if all the substances adsorbed are really liquidified in the capillaries, all these curves should coincide, regardless of temperature. That the water content of the gel has practically no effect, is seen by the values for butane at

30° with gels of three different water contents. These three curves coincide.

When we make the statement that these curves should all coincide, it must be remembered that this is made under the assumption that the physical properties of a liquid in a capillary are the same as with the liquid under ordinary conditions, inasmuch as r is calculated by formula (10) which involves surface tension, density and molecular weight. That these properties suffer no change in a capillary is probably not the case.

Let us ask the question now: What factors would it be possible to change in order to bring these curves together? Considering, for^{the} nonce, the curves as they exist at the lower volumes (say below $V = .2$ cc), it is seen that any factor which increases r or decreases V more at high temperatures than at low, would tend to bring the curves closer together. V itself is calculated by the use of one factor only, that is density. If we postulate that the density is less in the capillary (i.e. that we have a decrease in internal pressure or pull upwards), then the volume would be greater, - but at the same time, since the density term occurs in the denominator of equation (10), the radius would also be greater. With this dual effect of density, it is hard to predict what the sum total effect of a lower density would be on the curves.

Moreover, it can be shown that the change of density with moderate changes of pressure, such as we would expect from the capillary forces, is small. This prediction is based on the calculation that the compressibility of the liquid is independent of the direction of change of internal pressure.

If we postulate solubility of the substance in the water of the gel, this gives us a wrong correction, since the correction applied to V would be less at high temperatures than at low.

Should non-liquefaction be postulated, we again come into difficulty, inasmuch as at high temperatures there would be more non-liquefaction than at low, and therefore a greater volume correction increase at higher temperatures than at low.

Possible polymerization in the capillaries does not bring us near the solution of the problem, inasmuch as the effect would be much greater at low temperatures than at high, and therefore, since it occurs in the numerator of equation (10) r would be corrected more at low temperatures than at high, and the curves would be still farther apart.

An increase in the size of the pores would give us the proper correction, but it is hard to imagine that the gel structure changes sufficiently over the temperatures used. Gels can be heated over 300°C . for great lengths of time without changing their absorptive power or water content.

When we come to surface tension, however, we have a factor which no doubt causes much of the trouble. Assuming a change in the surface tension of the liquid, two general influences may operate. First, for equal volumes adsorbed there is a greater pressure above the liquid in the capillary at the higher temperatures. Now, there being more molecules in the vapor phase, these would tend to attract the liquid molecules and decrease the surface tension. In order to roughly estimate this effect, let us assume liquid sulfur dioxide in contact with its vapor at two different temperatures where the same volume is adsorbed (giving same sized capillaries). In these two systems, the pressure over the liquid at the higher temperature is obviously much greater. From these corresponding pressures, calculate the concentration in moles per litre of the gaseous phase. Also calculate the concentration in moles per litre of the liquid phase (knowing density and molecular weight). As the pressure above the liquid becomes greater and greater, the surface tension becomes less and less, until, when the concentration of the vapor is equal to that of the liquid, the surface tension is, obviously, zero. Now plot the surface tension against the concentration, in moles per litre, of the gaseous phase. The results of this calculation with sulfur dioxide at 50° and 100° are given in graph II and table III.

Conc. i
mole/l
litre
gas
phos.

1

25

50

75

100

125

20

40

60

80

100

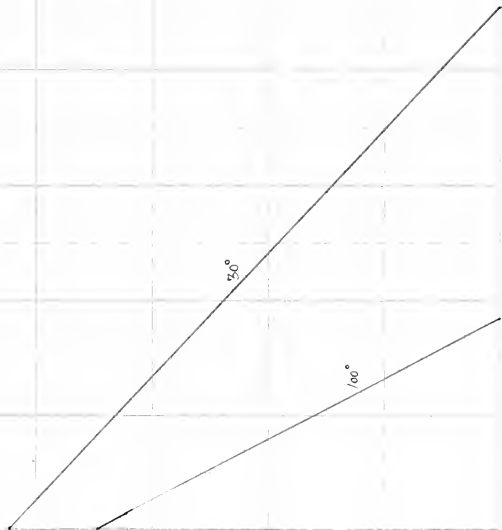


TABLE III

Temp.	P (cm)	C (mols litre)	C (mols litre)	~ (assumed in vacuo)
50°	349.6	.00018	21.18	22.75
100°	2114.3	.00090	17.36	9.25

By an inspection of the curves, one sees that a comparatively small concentration in the gaseous phase of .0009 mols litre would lower the surface tension only to an infinitesimal extent.

This leaves the fact that the surface tension must be different solely on account of the capillary effect itself. This is extremely probable; for, if condensation does take place in a capillary at a pressure below the ordinary saturation pressure, it follows that the critical temperature in a capillary is higher. If the critical temperature of a substance is raised, the surface tension must correspondingly be raised, inasmuch as the temperature - surface tension function cuts the temperature axis at the critical temperature.

This raised effect of surface tension would much more than counterbalance the very small pressure effect before described which works ~~oppositely~~. Furthermore, this correction

is in the right order, for σ occurs in the numerator of equation (10), and thus the radii would be greatly increased. It is hard to say whether this effect (for equal volumes - or equal capillary environment) would be greater at low or high temperatures. If a straight line function between σ and T is assumed, it looks as if the correction would be independent of the temperature. This will be considered later under the subject of the critical solution temperature.

However, that the radii would come out larger is an indication of the correctness of the above assumption, since it has always been hard to harmonize capillary condensation in tubes which are very near to atomic dimensions.

The conclusion of the above considerations of the V - r curves is that the density or, more important, the surface tension of a liquid is different in a capillary tube than on a plane surface.

It is now apparent that it would be futile to combine equation (10) with some general assumed V - r relationship, since the V - r curves are so far apart and the final equation would be burdened with too many constants by virtue of the fact that a cubic equation would have to be used to relate V and r throughout the entire range.

In order to solve for S_0 , therefore, in the following experiments with adsorption of water from butyl alcohol, V_{H_2O} will be found experimentally, and from it a value of r according to the water vapor curve (Graph I), which will be assumed to represent the true state of affairs, inasmuch as we are here also dealing with water. From this value of r , S_0 will be found by the equation

$$\log \frac{S_0}{S} = \frac{2.303 \log^{7(.1343)}}{D_0 R T r} \text{ -----(11)}$$

EXPERIMENTAL

n-Butyl alcohol and water were used because these liquids are miscible in each other to the extent of about 20%. In experiments hitherto made, adsorption has been studied with liquids miscible in all proportions. The latter, of course, will give a value of S_0 , as will be seen below, but this could not be compared with any existing finite value of solubility, - that is, there would be no definite saturation concentration.

The general procedure followed consisted of treating solutions of known concentration of water in butyl alcohol - ranging from zero to about fifteen percent water - with a certain amount of gel, and, after equilibrium was attained, analyzing the solution for water to determine the equilibrium concentration as well as the amount of water taken up per gram of gel.

The gel was prepared as usual, and a granular form used which passed through a 12 and was retained by a 16 mesh sieve. The water content was determined by heating to constant weight, and found to be 5.2%. This gel was kept in a well stoppered separatory funnel arranged for delivery into a narrow mouthed flask which contained the solution. The same gel was used throughout the following experiments, and was kept in a desiccator.

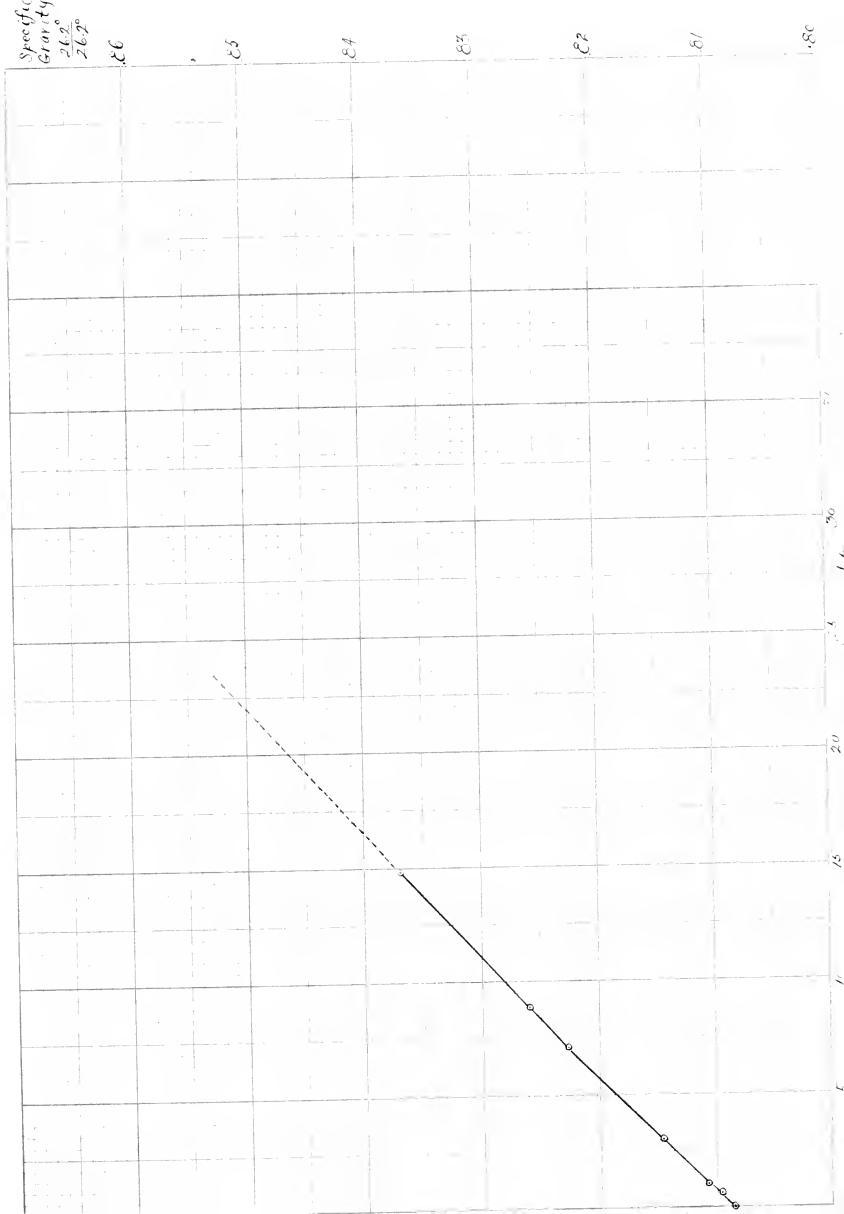
n-Butyl alcohol was obtained from the Commercial Solvents Company, and fractionated to remove the water. The fraction taken was that boiling between 114.2° - 114.6° at 770.5 mm. pressure, according to the vapor pressure curve given by Landolt-Börnstein. The method of analysis used was the determination of the specific gravity of the aqueous-alcoholic solution by means of an

Ostwald pycnometer. Solutions of varying water content up to about fifteen percent were made up by weighing, and the specific gravity of these solutions determined, giving the curve represented in Graph III. The pycnometers were immersed in a thermostat controlled to $.05^{\circ}\text{C}$. until constant volume of the liquid. The checks given below were always made using a different pycnometer for a solution. The "specific gravities" determined are referred to water at 20.2° - the temperature of the thermostat used.

TABLE III

Weight Flask	+ H ₂ O	+ BuOH	% H ₂ O	Mt. sol. in pyknom.	Mt. water in same pyknom.	sp. gr.	sp. gr.
24.5580	25.0562	74.5365	1.00	8.1129 4.0499	10.0080 4.9960	.81066 .81066	.81066
28.3097	31.9565	79.5057	7.12	8.1835 4.1099	9.9460 4.9960	.82263 .82264	.82266
27.4695	34.8865	77.6084	14.79	4.1814 8.3755	4.9960 10.0080	.83695 .83690	.83693
27.6961	27.9759	77.8327	0.56	8.0522 8.1020	9.9460 10.0080	.80958 .80955	.80957
24.5436	26.0519	74.6411	3.01	4.0700 8.1550	4.9960 10.0080	.81465 .81467	.81466
28.3156	32.7656	78.5322	8.86	8.2664 4.1269	10.0080 4.9960	.82600 .82604	.82602

These values are given on the Graph, which would have to be much enlarged in order to read off accurately the percentage of water from the specific gravity determined. The graph is given merely in order to determine some other values later on by extrapolation.

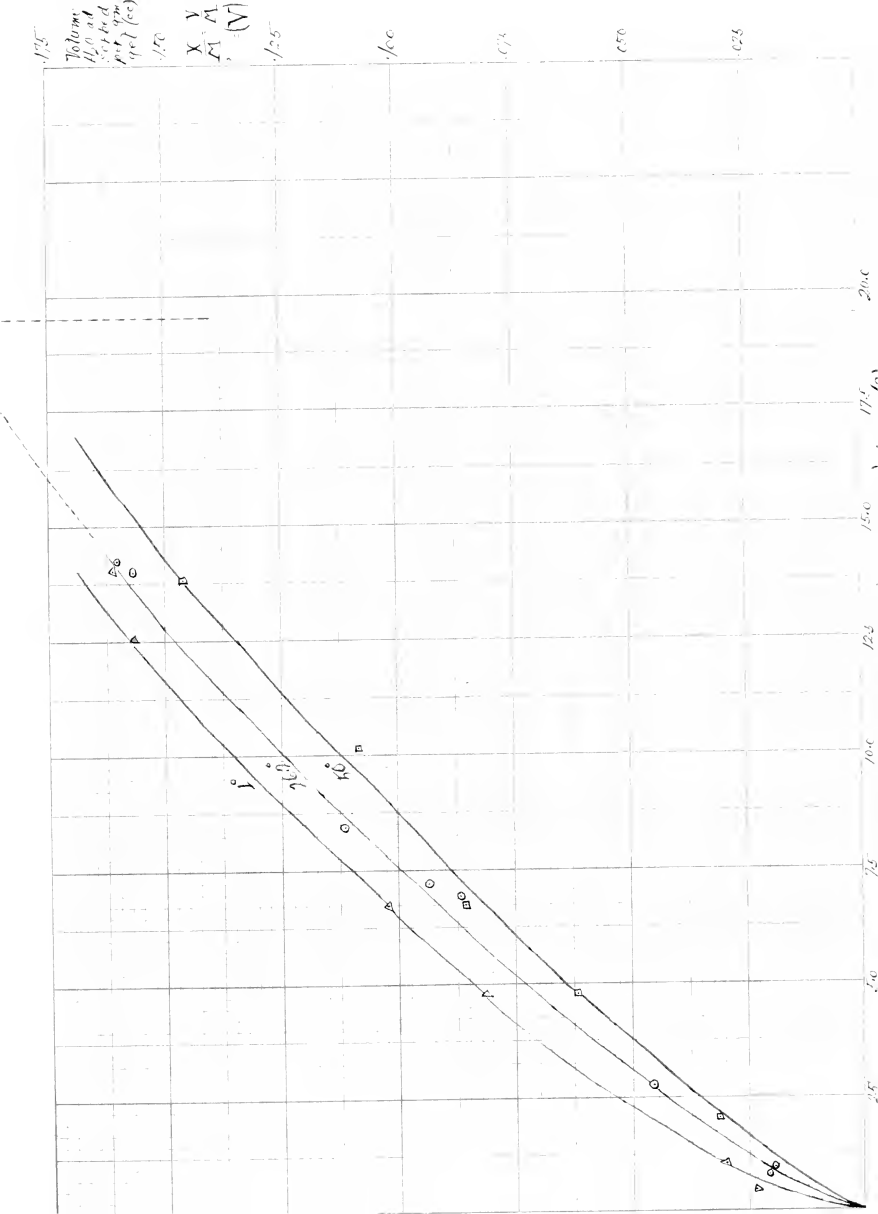


Experiments were now made at 1° , 25.2° , 50° of adsorption of the water by the silica gel. The flasks were allowed to remain at the temperature, with very frequent shaking, for at least four hours. Determination of specific gravity after this time showed that four hours was more than sufficient time for equilibrium to be attained. The liquid was then carefully sucked into the weighed Ostwald pycnometer, immersed in the thermostat until constant volume, and weighed. The results are given in detail in the following tables. For the curves, the equilibrium concentrations in percent were plotted against the grams of water adsorbed per gram of gel.

TABLE IV

35.2°							
Gms. solu.	Gms. H ₂ O present in solu.	Gms. gel added	sp. gr. eg. mixture (checked)	% H ₂ O from Curve	Gms. H ₂ O at End	Gms. H ₂ O Adsorb.	$\frac{X}{m} = \frac{V}{m}$
33.3598	0.3083	1.4673	.81028	0.83	0.2769	.0314	.0214
33.3754	0.9757	1.1967	.81413	2.76	0.9212	.0545	.0455
20.2582	1.7361	1.5284	.82296	7.24	1.0115	.1546	.0938
33.4693	2.9753	1.3526	.82511	8.44	2.8248	.1505	.1113
33.5144	4.9708	1.2144	.83600	14.25	4.7757	.1951	.1607
33.3741	0.3231	1.3664	.81043	0.92	0.3070	.0261	.0191
34.2538	2.4888	1.4402	.82226	6.90	2.3635	.1253	.0870
33.5793	4.9856	1.8097	.83551	14.00	4.7009	.2347	.1573

Pure butyl alcohol was found to have a specific gravity of
 .80950 ^{26.2}_{7.5}



For 1° and 50°, data is given in the following table.

TABLE V

Temp.	% H ₂ O eq.	$\frac{r}{m}$
1°	6.75	.1020
1°	0.40	.0235
1°	1.05	.0300
1°	4.80	.0812
1°	14.04	.1620
1°	12.60	.1568
50°	6.75	.0859
50°	4.83	.0618
50°	2.10	.0314
50°	10.17	.1083
50°	13.87	.1460

The results are plotted in Graph IV. Only the results at 20.1° are of much value, however, for the calculation of β_0 , since the V-r water vapor curve, of Graph I, was determined for 30°.

Now, values of $\frac{r}{m}$ from table IV (which can be assumed equal to $\frac{V}{m}$ for this calculation) are applied to the water vapor curve, and values of r corresponding are found, from which in turn β_0 can be calculated by equation (11).

Before concluding the experimental part, some few further determinations must be described which will be used later in the calculations.

Solubility data of n-butyl alcohol and water could not be found in the literature, so this was determined by the specific gravity method as above. Water and butyl alcohol were allowed to stand in contact with each other at 1° and 26.2° for several hours with frequent shaking. After equilibrium was attained, a sample of the butyl alcohol layer was pipetted off and tested for specific gravity.

TABLE VI

Butyl Alcohol Layer

Temp.	sp. gr.	% H ₂ O
1°	.84530	17.8
26.2°	.84614	19.5

An approximate value for the critical solution temperature was determined by heating some butyl alcohol and water in a closed tube in a bath until the alcohol - water meniscus disappeared. The tube was then shaken and allowed to cool slowly in a bath with an accurate thermometer until the first haziness appeared, when the temperature was noted. This was found to be 134.8° - very close to the value for iso-butyl alcohol (131.5°). This is to be expected, inasmuch as the physical

properties in general of normal and iso-butyl alcohols are very similar; whereas the secondary has quite different physical properties.

CALCULATIONS.

In order to calculate S_0 , we use the equation before derived:

$$\log \frac{S_0}{S} = \frac{2 M \sigma 10^7 (.4345)}{D_0 R T r}$$

The question naturally arises, what value are we to use for σ , the surface, or, in this case, the interfacial tension. There are two possibilities, depending upon whether we assume the water separating out in the capillaries is pure water or water containing a certain amount of dissolved butyl alcohol.

We have the relation ²

$$\gamma_{B.W.} = \gamma_{W'} - \gamma_{B'} \quad (12)$$

where

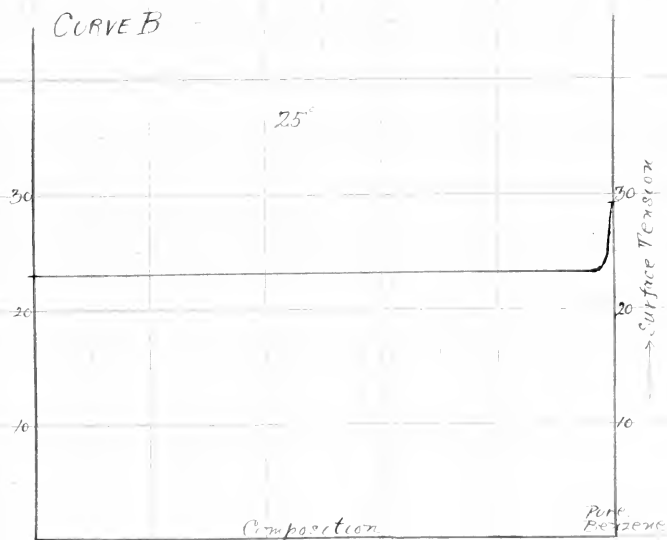
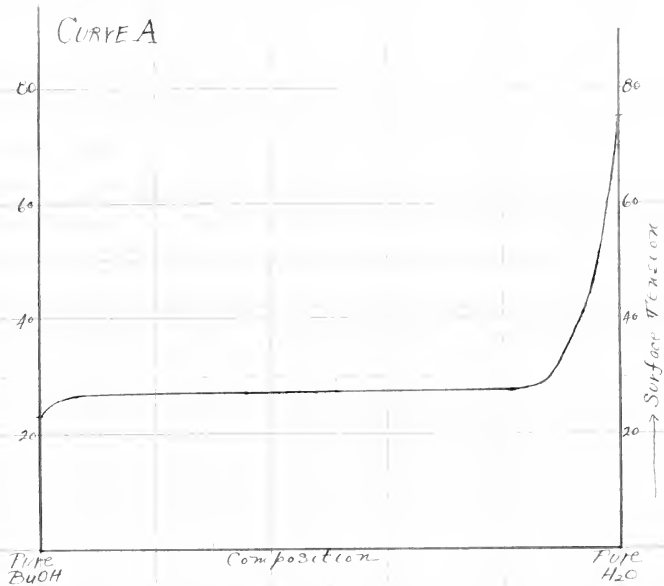
$\gamma_{B.W.}$ = interfacial tension of butyl alcohol and water

$\gamma_{W'}$ = surface tension of water saturated with butyl alcohol

$\gamma_{B'}$ = surface tension of butyl alcohol saturated with water.

We also know that a capillary active substance lowers the surface tension much more than a capillary inactive substance

1. Freundlich - Kapillarchemie, p. 152.





raises it. This condition is generally represented by the curve A on graph V (1).

According to the curve, then, and equation (12) if the phase which separates out is pure water, then σ_{pw} will be approximately 75 - 25 say or about 50; but if the phase is water containing its dissolved butyl alcohol, then the interfacial tension would be say, about 50 - 25 or about 5.

Which value to use becomes very evident upon consulting the values in table IV, which represent the amount of water removed by the adsorption. In all cases, this is very slight, amounting to about .2 gram of water from a solution containing 5 grams of water (see last experiment, table IV). This indicates that the interfacial tension must be very small indeed, else much more water would be removed. Hence we are justified in assuming that the water in the gel - at least at the surface of the pore - contains its quota of dissolved alcohol. Unfortunately, however, the surface tensions σ_w^l and σ_s^l have not been worked out. In lieu of this, and the fact that iso butyl alcohol is very similar to n-butyl alcohol, we will use Antonow's ¹ value of the interfacial tension (σ_{sw}) 1.76. We will use 1.8 for σ in our formula.

1. Antonow - J. d. Chim. Phys. 5 372, 1907

The values used to calculate S_0 according to equation (11) are:

$$M = 18$$

$$\gamma = 1.8$$

$$D_0 = 1$$

$$R = 8.3 \times 10^7$$

$$T = 298$$

$$r = \text{see table following}$$

$$S = \text{equilibrium concentration of } H_2O \text{ from table IV.}$$

TABLE VII

25°

$\frac{V}{m}$ (table IV)	$r(\%)$ From Graph I H ₂ O curve	S (table IV)	$\log \frac{S_0}{S}$	$\log S$	$\log S_0$	S_0
.0214	.23	0.83	.04977	1.91909	1.96785	0.929
.0455	.55	2.76	.03205	0.44091	0.47296	2.971
.0958	.56	7.24	.02003	0.85974	0.87977	7.532
.1113	.65	8.44	.01781	0.92634	0.94415	8.793
.1607	.87	14.25	.01289	1.15381	1.16670	14.686
.0191	.21	0.92	.05342	1.96379	0.01721	1.040
.0870	.53	6.90	.02117	0.85885	0.86002	7.245
.1573	.65	14.00	.01320	1.14613	1.15933	14.453

From this table it is seen that S_0 is not a constant, but increases regularly with the equilibrium concentration. However, in all cases, it is less than the saturation value, which has been determined at 26.2° and found to be 19.5% (See table VI). That is to say, as we have explained in the theoretical considerations, the "solution power" of butyl alcohol for water is less than would be indicated by the amount of water as given

by the usual solubility -19.5%.

Before discussing the various factors affecting this "constant", another calculation must be made. Inasmuch as the theoretical formula is entirely new, and complicated with so many factors, it was decided to calculate S_0 by the old empiric adsorption formula of Patrick and McGavack:

$$V = K \frac{(Sc)^{\frac{1}{n}}}{S_0}$$

However, since we have three unknowns in this equation: K , S_0 , $\frac{1}{n}$, we must resort to the following mathematical treatment.

Putting the equation in logarithmic form, we have

$$\log V = \frac{1}{n} \log (Sc) + (\log K - \frac{1}{n} \log S_0) \quad \text{---(13)}$$

where, if we plot $\log V$ against $\log (Sc)$, a straight line should be obtained with a slope of $\frac{1}{n}$ and an intercept on the $\log V$ axis of $(\log K - \frac{1}{n} \log S_0)$. The following table gives this calculation. The volumes (V) and concentrations (S) are read from the curve at 25° on Graph IV.

TABLE VIII

$\mu = 2$		$T = 25^{\circ}$		
V	$\log V$	$S(\rho)$	$S\sigma$	$\log(S\sigma)$
.025	1.60200	1.15	2.20	0.36173
.050	1.60103	2.12	3.24	0.79518
.075	1.12494	5.26	10.50	1.02119
.100	1.00000	7.65	13.30	1.13469
.125	1.00309	10.20	20.40	1.30963
.150	1.32391	12.00	23.00	1.11497

For 1° and 50° the values of $\log V$ and $\log S_0$ taken from the curves are:

TABLE IX

 $\phi = 2.3$ at 1° $\phi = 1.5$ at 50°

Temp.	$\log V$	$\log S_0$
1°	$\bar{1}.60800$	0.42222
1°	$\bar{1}.30103$	0.41510
1°	$\bar{1}.12404$	1.10037
1°	$\bar{1}.00000$	1.27600
1°	$\bar{0}.90309$	1.41132
1°	$\bar{0}.82391$	1.52114
50°	$\bar{1}.60800$	0.33219
50°	$\bar{1}.30103$	0.75051
50°	$\bar{1}.12404$	0.96537
50°	$\bar{1}.00000$	1.11628
50°	$\bar{0}.90309$	1.23147
50°	$\bar{0}.82391$	1.33041

The values of ϕ for 1° and 50° were approximated from the curve on Graph VIII, which see later.

The above values given in tables VIII and IX are plotted on Graph VI. S_0 is found as follows:

2.0
1.5
1.0
0.5

0

0.5

1.0

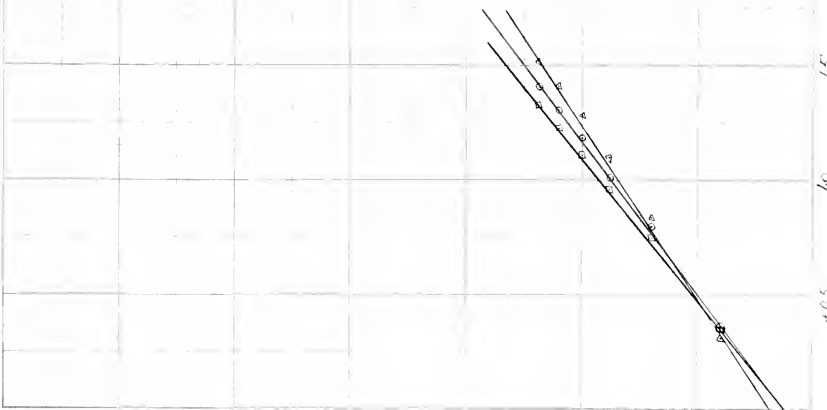
1.5

2.0

2.5

3.0

3.5



By measuring the slope from the curves, - for the 25° curve, we have

$$\frac{1}{n} = .767$$

Now we know that when $S = S_0$

$$V_0 = K\sigma^{\frac{1}{n}} \quad \text{or} \quad K = \frac{V_0^n}{\sigma^n}$$

where $V_0 = .2$ cc. approximately. This value .2 cc. is found by extrapolating the 25° isotherm on graph IV. If this is done, it is seen that when S is a concentration of 19.5%, the volume of water corresponding is about .2 cc. Now, according to table VI, 19.5% is the saturation value for butyl alcohol at 25° . It is to be expected that the conical capillaries will fill to different volumes, depending upon the value of the interfacial tension. Thus in the case of the system under consideration - that is, one in which the interfacial tension is very low - it is entirely probable that the capillary effect would cease at a smaller radius of the conical capillaries, therefore giving a less value for V_0 than with adsorption of a pure substance, such as sulfur dioxide. For purposes of approximation, however, we will proceed:

$$\text{Then } H = \frac{.2}{2^{.767}}$$

$$\text{Hence } \log H = \bar{0}.92986$$

and, from equation (15)

$$\bar{0}.92986 - .767 \log S_0 = -1.9$$

where -1.9 is the measured intercept on the curve.

$$\text{Hence } S_0 = 18.83$$

Similar calculations on the two other curves give data expressed in the following table (using $V_0 = .1$ throughout).

TABLE X

Temp.	$\frac{1}{n}$	$\log H$	S_0
1°	.665	$\bar{0}.94635$	17.74
25°	.767	$\bar{0}.92986$	18.83
50°	.815	$\bar{0}.84213$	20.14

$$\text{Av} = 18.92$$

This gives us a more "constant" value of 18.92 still less than the ordinary solubility - 19.5, .

THEORETICAL CONSIDERATIONS

In order to see what value σ_0 would have for liquids miscible in all proportions, data on the adsorption of n-butyl alcohol from benzene¹ was used to substitute in equation (11).

In this system, the butyl alcohol is adsorbed. Inasmuch as butyl alcohol lowers the surface tension of benzene, the butyl alcohol layer - containing some benzene - which separates out in the pores will have a surface tension of $\sigma'_{Bw} = 23$ approximately, - the ordinary surface tension of butyl alcohol (See Graph V). Assuming curve B on Graph V to represent the surface tension for benzene ($\sigma = 29.4$) and butyl alcohol ($\sigma = 23$), we can estimate the interfacial tensions σ'_{Bw} at various concentrations - as given in the table below.

TABLE VI

sp. gr. BuOH = .81

S(%)	σ_B	σ'_{Bw}	σ_{Bw}	$\frac{X}{m}$	$\frac{V}{m}$	r()
0	29.4	29.4	29.4	.026	.052	.28
.05	29.4	29.4	29.4	.056	.069	.45
.35	28.7	28.7	28.7	.066	.082	.51
.97	24.7	24.7	24.7	.104	.129	.70
2.55	23.3	23.3	23.3	.126	.156	.85
5.90	23.3	23.3	23.3	.128	.159	.87

r is taken as usual from water vapor results on graph I. From the values of r and γ , S_0 is calculated according to equation (11), - results given in next table.

TABLE III

$\log \frac{S_0}{S}$	$\log S$	$\log S_0$	S_0
6.75195	-----	-----	-----
0.45545	2.69887	9.15442	0.1427
0.25252	1.54407	9.77639	0.5976
0.07777	1.98677	0.05454	1.1600
0.01150	0.40654	0.41714	2.6170
0.01104	0.77085	0.76180	5.6520

Here, we see that, although benzene and butyl alcohol are miscible in all proportions, we obtain a definite value for S_0 by no means near infinity !

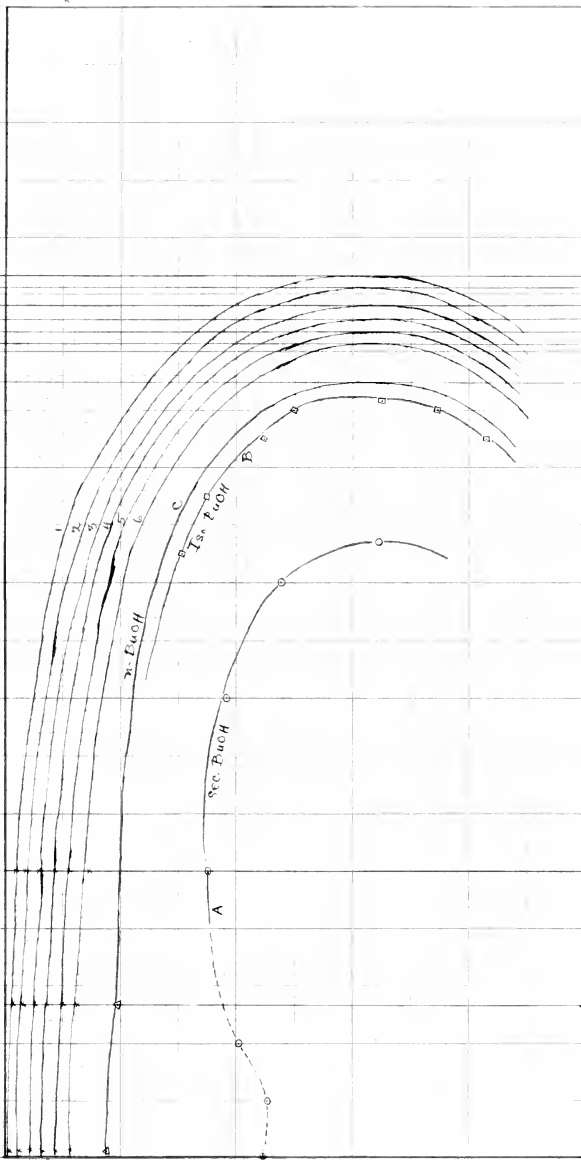
Considering again the values of S_0 given in table VII, one notices that there is a constant variation in proportion to the equilibrium concentration. From the factors bearing on the equation used to calculate S_0 - as discussed in the theoretical consideration under sulfur dioxide - the most probable quantities which tend to make S_0 not constant are un-

doubtedly surface tension and density. Inasmuch as density affects both sides of the equation, i.e. since it is used to calculate both r and β_0 , it is difficult to predict the direction of a correction applied to it. The surface tension, however, is without doubt greater in capillaries, inasmuch as condensation takes place below the saturation pressure. That is to say, the critical temperature in a capillary system must be higher in order to have this capillary condensation. Now, if the critical temperature is higher, the surface tension must be higher, according to the ordinary σ - T curves. An idea of how this increase in surface tension may be approximately estimated, is given by the following discussion:

According to table VI, the amount of water at saturation in butyl alcohol at 1° and 25° is 17.6 and 19.5 % respectively. These two points on a T - composition diagram are plotted on Graph VII, as a and b. Curve B represents the phase relationships for iso butyl alcohol, and curve A for sec. butyl alcohol, the data being taken from Landolt - Börnstein. Iso butyl alcohol has a C. S. T. of 131.5° , sec. butyl of 107° and we have estimated that of n-butyl to be 134.8° - point c. Connecting points a, b and c in a smooth curve similar to that of iso butyl alcohol, we obtain the curve desired - Curve C.

Now according to the curves on Graph IV, let us read off

Pure PuOH



Pure H_2O

the equilibrium concentrations corresponding to $\frac{X}{M}$ or $V = .025$, .05, .075, .100, .125 and .150 - for the three curves. The equilibrium concentrations (δ H₂O) read as abscissae for $\frac{X}{M} = .025$ give us three points, which, if plotted on Graph VII, give us curve 1. Now, this curve, when drawn parallel to the ordinary curve C, represents the phase conditions which would result if changes are produced in capillaries which correspond to a volume adsorbed of .025 cc. Likewise, for $\frac{X}{M} = .05$, three more points are obtained giving curve 2 for somewhat larger capillaries. We thus obtain the series of curves as drawn. Tangents to these curves, parallel to the composition axis will cut the temperature axis in points which should be the critical solution temperatures obtained in the capillary systems. For the smallest capillary value, corresponding to an $\frac{X}{M}$ of .025 cc., 155° is obtained as the new critical temperature.

In Graph VIII, Curve A represents the σ -T curve for n-butyl alcohol and water. This curve was drawn between

$\gamma = 1.8$ at 25° and $\gamma = 0$ at 134.8°, the C. S. T. Plotting our new value for the C. S. T. and drawing curve B parallel to curve A, we find our new value of γ to be 2.5.

If this correction be applied to recalculate δ_0 , only a very slight change is produced; but this is because the interfacial tension was only very small to begin with. With substances showing a high surface or interfacial tension under

T_{total}
 T_{actual}
 $\eta_{c, max}$
 (C_{PW})

μ

μ

μ

Cure B

Cure A

ordinary conditions, the correction to apply would be much larger. In case of gaseous adsorption, a similar method as above could^b applied, using the T-density curve instead of the T-composition curve.

BIOGRAPHY

Norman Fitzhugh Nerman was born February 22, 1896 at Lancaster, Pa. He obtained the B. S. degree at Franklin and Marshall College in 1918 and the M. S. degree at the University of Maine in 1921. From 1919 to 1921, he held the position of Instructor in Chemistry at the University of Maine. During the war, he was employed by the General Chemical Company at Laurens Hook, Pa. as chemist in the manufacture of sulfuric acid by the contact process. While working for the Doctor's degree at the Johns Hopkins University, he held an assistantship in undergraduate chemistry for two years.

